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Patent No. 571,792

## Process for Printing Textiles and Printing Preparations Therefor

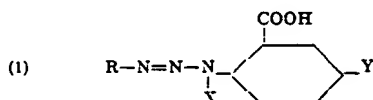
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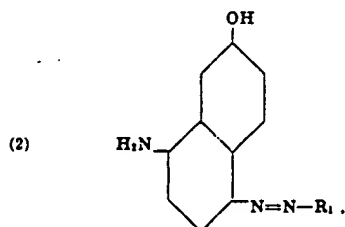
12 Claims—No drawing

The present invention is based on the observation that valuable prints on textiles can be produced by printing on the textile a coupling component and a stabilized diazo-compound followed by development of the dyestuff under neutral conditions such as by steaming with neutral steam, if there is used a printing preparation which contains as coupling component a 4-arylo-1-amino-7-hydroxynaphthalene free from groups imparting solubility in water and as stabilized diazo-compound a diazoamino-compound of the formula



in which R represents an at most bicyclic aryl radical free from groups imparting solubility in water, X represents a hydrocarbon radical which may contain a group imparting solubility in water, and Y represents a hydrogen atom or a sulfonic acid group.

As examples of 4-arylo-1-amino-7-hydroxynaphthalenes there may be mentioned, for example, 4- $\alpha$ -naphthylazo-1-amino-7-hydroxynaphthalene, and especially 4-arylo-1-amino-7-hydroxynaphthalenes of the formula



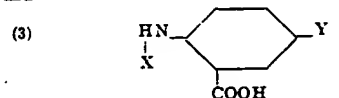
in which R<sub>1</sub> represents a naphthalene radical which may be substituted or advantageously a benzene radical. The coupling components of the formula (2) can be made by methods in themselves known, for example, by coupling 1-amino-7-hydroxynaphthalene in a strong to weakly acid medium with a diazotized aminonaphthalene or aminobenzene derivative, such as

$\alpha$ -Naphthylamine,  
6-methoxy-2-aminonaphthalene,  
2-nitro-1-aminobenzene,  
2-methoxy-5-chloro- or 4-nitro-1-aminobenzene,  
2-methyl-4-chloro- or 4-nitro-1-aminobenzene,  
2:5-dimethoxy-4-benzoylamino-1-aminobenzene,  
2-chloro-5-trifluoromethyl-1-aminobenzene,  
2-nitro-4-methoxy-1-aminobenzene,  
2:5-dichloro-1-aminobenzene,  
2:5-dimethoxy-4-nitro-1-aminobenzene,  
2-methoxy-4-chloro-5-methyl-1-aminobenzene,  
2:5-dimethoxy-4-chloro-1-aminobenzene,  
2-nitro-4-methyl- or 2:5-dinitro-1-aminobenzene and

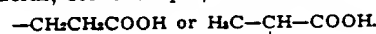
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2-methyl- or 2-methoxy-1-aminobenzene-5-sulfonic acid amides, such as 2-methyl-1-aminobenzene-5-sulfonic acid diethylamide.

The diazoamino-compounds to be used with the aforesaid coupling components for making the printing preparations to be used in the process of this invention can be obtained by methods in themselves known, for example, by condensing a diazotized at most bicyclic aromatic base, which is free from groups imparting solubility in water, with an aminobenzene carboxylic acid of the formula



in which Y represents a hydrogen atom or a sulfonic acid group, and X represents a hydrocarbon radical which may contain a group imparting solubility in water, especially a carboxylic acid group. As such hydrocarbon radicals there may be mentioned, for example, methyl, ethyl, propyl, benzyl, isopropyl and isobutyl groups, and also the radicals of carboxylic acids, for example, the radical



As examples of compounds of the formula (3) there may be mentioned:

1-methylaminobenzene-2-carboxylic acid-4-sulfonic acid,  
1-benzylaminobenzene-2-carboxylic acid-4-sulfonic acid,  
1-ethylaminobenzene-2-carboxylic acid-4-sulfonic acid,  
1-isopropylaminobenzene-2-carboxylic acid-4-sulfonic acid,  
1-butylaminobenzene-2-carboxylic acid-4-sulfonic acid,  
1-isobutylaminobenzene-2-carboxylic acid-4-sulfonic acid,  
 $\alpha$ -(2-carboxyphenylamino)-propionic acid,  
 $\alpha$ -(2-carboxyphenylamino)-butyric acid,  
 $\alpha$ -(2-carboxyphenylamino)-valeric acid,  
 $\alpha$ -(2-carboxyphenylamino)- $\beta$ -methylbutyric acid and  
 $\alpha$ -(2-carboxyphenylamino)-phenyl-acetic acid.

As diazo-compounds to be condensed with the aforesaid compounds of the formula (3) there may be mentioned, for example, the diazo-compounds obtainable by methods in themselves known from the following aromatic bases:

$\alpha$ -Naphthylamine and especially 2:5-dichloraniline,  
2:5-dimethoxy- or 2-methyl-5-chloraniline,  
2-methoxy- or 2-methyl-4-nitroaniline,  
2:5-dimethoxy-4-benzoylamino-1-aminobenzene,  
2:5-diethoxy-4-benzoylamino-1-aminobenzene,  
2-methoxy-5-methyl-4-benzoylamino-1-aminobenzene,  
1-aminobenzene-3-sulfonic acid piperidine,  
1-amino-2-methoxybenzene-3-sulfonic acid diethylamide,  
1-amino-2-methylbenzene-3-sulfonic acid diethylamide,  
1-amino-2-methylbenzene-3-sulfonic acid dimethylamide,  
1-amino-2-methylbenzene-3-sulfonic acid morpholide,  
1-amino-2-methyl- or -methoxybenzene-3-sulfonic acid piperide.

The condensation is advantageously carried out in an alkaline medium, and the alkali metal salts of the diazoamino-compounds so obtained can easily be isolated by methods in themselves known, for example, by salting out or by subjecting solution thereof, if desired, after filtering them, to a rapid drying operation.

The printing preparations are prepared from the aforesaid components with the solvents and thickening agents usual for such preparations. Advantageously, there are used in the process of this

invention printing preparations of the aforesaid kind, which contain free alkali metal hydroxide, for example, sodium hydroxide or potassium hydroxide.

By the process of this invention fabrics or mixed fabrics, especially those of cellulose fibers, are printed by known methods, for example, by screen printing or roller printing. Strong prints are obtained by steaming with neutral steam and also in most cases by steaming with acid steam. In many cases the printed fabrics, which have been dried in the usual manner, can also be developed by heating them at a temperature above 100°C, and advantageously 130-150°C. This heating may be carried out, for example, in chambers heated electrically or by other means, and without supplying steam. For this purpose a small proportion of a hydrophilic substance, for example, glycerine must be added to the printing paste.

Solutions obtained by replacing by water 70-100% of the thickening agent present in a printing paste can be used for padding fabrics or mixed fabrics,

especially those of cellulose fibers, by the customary methods, for example, on a 2-roller foulard. The dyed fabrics are then dried at 50-60°C and, as described above for printing, subsequently developed by neutral or acid steaming or by dry heat treatment at a temperature above 100°C.

By using the customary preprinting or over-printing methods white or colored reserves can be produced on materials dyed in the manner described above.

In many cases the printing yield can be somewhat improved if, before drying, the printed material is treated for 30-60 seconds in a bath, especially an acid bath, containing bichromate, for example in a bath containing per liter, 2 grams of sodium bichromate and 3-5 grams of acetic acid of 40% strength. This treatment is especially advantageous when the printing paste has been allowed to stand for quite some time.

The following Examples illustrate the invention, the parts and percentages being by weight:

#### EXAMPLE I

IN THIS EXAMPLE THERE ARE USED THE FOLLOWING PRINTING COLORS OF WHICH 100 PARTS HAVE THE FOLLOWING COMPOSITIONS:

	Diazamino-compound obtained from		Titre	Parts	Coupling Component	Parts	Sodium sulfate	Sodium diisopropyl-naphthalene sulfonate	Tint of print so obtained
	Base	Stabilizer							
A	1-Amino-2-methoxy-4-nitrobenzene	1-isobutylamino-benzene-2-carboxylic acid-4-sulfonic acid	60%	64.0	1:7-amino-naphthol-4:1'-azo-2'-methoxy-5'-chlorobenzene	27.8	7.2	1.0	dark olive
B	"	"	60%	62.0	1:7-amino-naphthol-4:1'-azo-2':5'-dichlorobenzene	27.3	9.7	1.0	reddish black
C	1-Amino-2-methoxy-5-chlorobenzene	1-ethylamino-benzene-2-carboxylic acid-4-sulfonic acid	60%	58.5	1:7-amino-naphthol-4:1'-azo-2'-methoxy-4'-nitrobenzene	28.7	11.8	1.0	black
D	1-Amino-2-methyl-4-nitrobenzene	$\alpha$ -(2-carboxy-phenyl)-amino-valeric acid	50%	67.2	1:7-amino-naphthol-4:1'-azo-2'-methoxy-4'-nitrobenzene	28.4	3.4	1.0	brownish black
E	1-Amino-2-methoxybenzene-5-sulfonic acid morpholide	1-Isobutylamino-benzene-2-carboxylic acid-4-sulfonic acid	58%	65.5	1:7-amino-naphthol-4:1'-azo-2'-methoxy-4'-nitrobenzene	23.2	10.3	1.0	black
F	1-Amino-2-methylbenzene-5-sulfonic acid diethylamine	1-isopropyl-aminobenzene-2-carboxylic acid-4-sulfonic acid	63%	62.1	1:7-amino-naphthol-4:1'-azo-2'-methyl-4'-chlorobenzene	23.8	13.1	1.0	grey brown
G	1-Amino-2-methoxy-5-chlorobenzene	1-ethylamino-benzene-2-carboxylic acid-4-sulfonic acid	60%	60.6	1:7-amino-naphthol-4:1'-azo-2'-methyl-4'-nitrobenzene	28.4	10.0	1.0	brownish black
H	1-amino-2-methyl-5-chlorobenzene	"	55%	62.9	1:7-amino-naphthol-4:1'-azo-2'-methoxy-4'-chloro-5'-methyl benzene	29.8	6.3	1.0	olive brown
J	1-Amino-2-methoxy-5-chlorobenzene	1-ethylamino-benzene-2-carboxylic acid-4-sulfonic acid	60%	58.0	1:7-amino-naphthol-4:1'-azo-2':5'-dimethoxy-4'-nitrobenzene	29.6	11.4	1.0	black
K	1-Amino-2-methyl-4-nitrobenzene	$\alpha$ -(2-carboxy-phenyl)-amino-valeric acid	50%	67.5	1:7-amino-naphthol-4:1'-azo-2'-methyl-4'-chlorobenzene	26.4	5.1	1.0	dark brown
L	1-Amino-2:5-dichlorobenzene	$\alpha$ -(2-carboxy-phenyl)-amino-phenyl-acetic acid	48%	69.7	1:7-amino-naphthol-4:1'-azo-2':4'-din nitrobenzene	26.9	2.4	1.0	brown
M	1-Amino-2-chloro-5-trifluoromethyl-benzene	$\alpha$ -(2-carboxy-phenyl)-amino- $\beta$ -methyl-butyric acid	48%	67.2	1:7-amino-naphthol-4:1'-azo-2'-nitro-4'-chlorobenzene	25.0	6.8	1.0	violet brown

## EXAMPLE I (continued)

IN THIS EXAMPLE THERE ARE USED THE FOLLOWING PRINTING COLORS OF WHICH 100 PARTS HAVE THE FOLLOWING COMPOSITIONS:

Diazoamino-compound obtained from		Titre	Parts	Coupling Component	Parts	Sodium sulfate	Sodium diisopropyl-naphthalene sulfonate	Tint of print so obtained
Base	Stabilizer							
N 1-Amino-2-methoxy-5-chlorobenzene	1-ethyl-aminobenzene-2-carboxylic acid-4-sulfonic acid	60%	63.0	1:7-amino-naphthol-4:1'-azo-naphthalene	28.6	7.4	1.0	brownish black
O 1-Amino-2-methylbenzene-5-sulfonic acid diethylamide	"	82%	45.9	1:7-amino-naphthol-4:2'-azo-6'-methoxy-naphthalene	25.9	27.2	1.0	olive brown

WITH THE ABOVE PRINTING COLORS THERE ARE PREPARED PRINTING PASTES HAVING THE FOLLOWING COMPOSITIONS:

	A	B	C	D	E	F	G	H	J	K	L	M	N	O
Printing color.....	100	120	100	120	120	120	120	80	120	120	120	120	120	120
Alcohol (denatured).....	50	50	80	60	60	80	60	50	50	60	60	60	60	80
Turkey Red oil.....	—	—	—	40	40	—	40	—	—	40	40	40	—	—
Urea.....	30	30	5	30	30	50	50	—	50	30	30	30	30	30
Sodium hydronide solution of 30% strength.....	25	30	30	25	25	30	30	25	30	30	30	30	30	25
Water.....	325	270	280	255	255	250	230	295	250	250	250	250	270	235
Neutral Starch-tragacanth thickening.....	450	450	450	450	450	450	450	530	450	450	450	450	450	450
Sodium chlorate (solid).....	10	10	—	10	10	10	10	10	10	10	10	10	10	10
Turpentine oil.....	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000

A cotton fabric is printed with the above printing pastes. The printed fabric is then dried at 50-60°C, and steamed neutral in a Mather-Platt steamer for 5-8 minutes at 100°C. The fabric is rinsed in the cold, and treated for 10 minutes at 40-50°C with an enzyme preparation in order to remove the starch. It is again rinsed in the cold, soaped at the boil for 10 minutes, and dried after being rinsed again. There are obtained full pure prints. The same printing yield can generally be obtained by means of dry heat, for example, when the fabric, which has been printed and predried in the usual manner, is developed by heating it at a temperature above 100°C, advantageously within the range of 130°C to 150°C, or by acid steaming for 2-5 minutes at 100°C, instead of neutral steaming. In many cases the printing yield can be somewhat improved by treating the printed material before it is dried for 30-60 seconds in a bath at 40°C which contains, per liter, 2 grams of sodium bichromate and 3-5 grams of acetic acid of 40% strength.

The diazo-amino-compound used for preparing the printing paste F may be prepared as follows:

24.2 parts of 1-amino-2-methylbenzene-5-sulfonic acid diethylamide are diazotized in the usual manner in 45 parts of hydrochloric acid of 10% strength and 30 parts of ice with 6.9 parts of sodium nitrite in 25 parts of water.

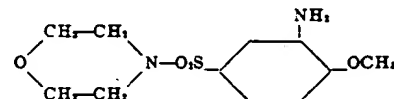
At the same time 28.5 parts of 1-isopropylamino-benzene-2-carboxylic acid-4-sulfonic acid are dissolved in 200 parts of water with the equivalent quantity of sodium hydroxide solution of 30% strength, and 60 parts of potassium carbonate are added. When dissolution is complete, the whole is cooled to 0°C, and the filtered diazo-solution is introduced dropwise in the course of 20 minutes while stirring well. After a short time the diazo-amino-compound crystallizes out in five lamellae and after 2 hours the coupling is complete. In order to complete the precipitation of the product 10 volumes per cent of sodium chloride are added, the whole is stirred for a further hour, and then the well crystallized precipitate is filtered off with suction. It is washed with a small amount of

saturated sodium chloride solution, pressed and dried in vacuo at 45-50°C.

The diazoamino-compound is obtained in good yield and has a content of 65-70% and is easily soluble in water.

The diazoamino-compound used for making the printing preparation E is obtained as follows:

A diazo-solution prepared in the usual manner from 27.2 parts of 1-amino-2-methoxybenzene-5-sulfonic acid morpholide of the formula



is added dropwise in the course of 20 minutes to a solution of 31.7 parts of the disodium salt of 1-isobutylaminobenzene-2-carboxylic acid-4-sulfonic acid, 2 parts of anhydrous sodium carbonate and 2 parts of sodium bicarbonate in 300 parts of water, cooled to 0 to -2°C. At the same time a sufficient quantity of sodium hydroxide solution of 30% strength is introduced dropwise to maintain the pH value of the mixture at 9.5 to 10. At the end the mixture is adjusted to a pH value of 10, filtered to remove a small amount of impurities and the solution is evaporated in a spray drier in which the inlet temperature of the air is between 130 and 180°C, and the outlet temperature is not less than 70°C and not substantially higher than 100°C.

The fine yellowish powder so obtained has a content of about 50% of diazo-amino-compound. The yield amounts to 80 to 85% of the theoretical yield.

## Example 2

A solution is prepared having the following composition:

Printing color C of Example 1.....	100 parts
Alcohol (denatured).....	80 parts
Urea.....	50 parts
Sodium hydronide solution of 30% strength.....	30 parts
Neutral tragacanth thickening (80:1000).....	100 parts
Water.....	640 parts
	1000 parts

A cotton fabric is padded with the above solution on a 2-roller foulard, and then squeezed and dried at 50-60°C. It is then steamed neutral for 5-8 minutes in a Mather-Platt steamer, rinsed in the cold, soaped at the boil for 10 minutes, again rinsed, and dried. There is obtained a full level black dyeing.

The same dyeing can also be produced by acid steaming for 2-5 minutes, instead of neutral steaming, or by heating the fabric for 5 minutes in an electrically heated chamber at 150°C.

#### Example 3

A white reserve can be produced by preprinting on a fabric dyed in accordance with Example 2, in the following manner:

A cotton fabric is printed with a printing paste consisting of

600 parts of a paste prepared from 274 parts of a powdered mixture of albumen, glue and gelatine and 326 parts of water.  
10 parts of calcined sodium carbonate.  
130 parts of water.  
20 parts of dimethyl-phenyl-benzylammonium chloride.  
200 parts of a mixture of 100 parts of zinc white and 100 parts of glycerine.  
40 parts of a mixture of 20 parts of titanium white and 20 parts of water.  
1000 parts.

The fabric is dried at 50-60°C and then foularded with a solution of printing color C as described in Example 2. By the further treatment described in that Example there is obtained a pure white effect on a black ground.

#### Example 4

The following printing pastes are printed side by side on a cotton fabric which has been padded as described in Example 2 and dried:

- (a) 150 parts of Ciba Scarlet G double extra paste (Color Index, 2nd Edition, 1956, Vol. II, page 2475, No. 73860) are stirred into 700 parts of a thickening of the composition given below, and then 90 parts of sodium formaldehyde-sulfoxylate and 60 parts of water are added.  
1000 parts
- (b) 90 parts of Cibacron Brilliant Green BF paste conc. (Color Index, 2nd Edition, 1956, Vol. II, page 2510, No. 59825) are stirred into 800 parts of a thickening of the composition given below, and then 80 parts of sodium formaldehyde-sulfoxylate and 30 parts of water are added.  
1000 parts.

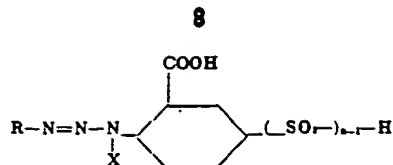
The thickening used in printing pastes (a) and (b) is prepared from

90 parts of wheat starch  
90 parts of cold water  
100 parts of glycerine  
140 parts of British gum powder  
170 parts of tragacanth mucilage (60:1000)  
170 parts of potassium carbonate  
240 parts of water  
1000 parts.

The printed fabric is dried at 50-60°C, and then steamed neutral in a Mather-Platt steamer for 5-8 minutes at 100°C. The material is then rinsed in the cold, treated with an enzyme preparation for 10 minutes at 40-50°C in order to remove the starch, then rinsed again, soaped at the boil for 10 minutes, rinsed again, and dried. There are obtained pure green and red prints on a black ground.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

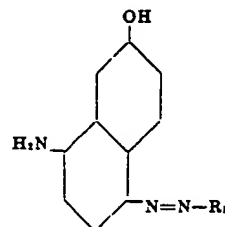
1. A preparation containing (A) a 4-aryl-azo-1-amino-7-hydroxynaphthalene free from groups imparting solubility in water and (B) a labile diazoamino compound of the formula



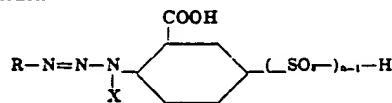
in which R represents an at most bicyclic aromatic radical free from water-solubilizing groups, n represents a whole number up to 2 and X a member selected from the group consisting of a hydrocarbon radical and a hydrocarbon radical bearing a water-solubilizing group.

2. A dyeing preparation according to claim 1, wherein the 4-arylazo-1-amino-7-hydroxynaphthalene is a 4-benzene-azo-1-amino-7-hydroxynaphthalene.

3. A printing preparation containing (A) a 4-aryl-azo-1-amino-7-hydroxynaphthalene of the formula

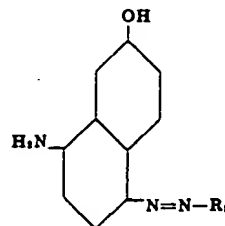


wherein R<sub>1</sub> represents a member selected from the group consisting of a naphthalene and a benzene radical, and (B) a labile diazoamino compound of the formula

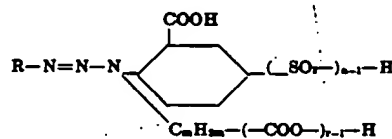


in which R represents an at most bicyclic aromatic radical free from water-solubilizing groups, n represents a whole number up to 2 and X an alkyl radical selected from the group consisting of branched and straight-chain alkyl radicals.

4. A printing preparation containing (A) a 4-aryl-azo-1-amino-7-hydroxynaphthalene of the formula

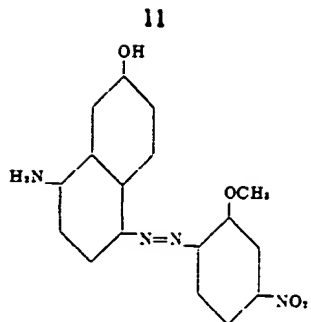


wherein R<sub>1</sub> represents a benzene radical containing a substituent which does not impart solubility in water, and (B) a labile diazoamino compound of the formula

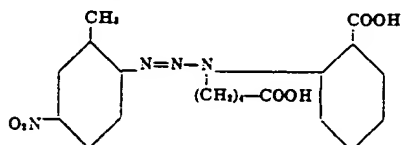


wherein n and r each represents a whole number up to 2, m represents a whole number up to 4 and R represents a benzene radical free from water-solubilizing groups.

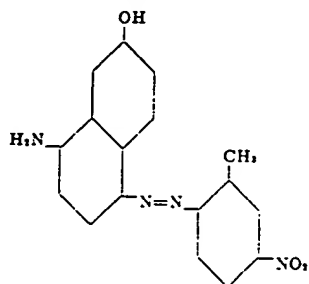
5. A printing preparation containing (A) a 4-aryl-azo-1-amino-7-hydroxynaphthalene of the formula



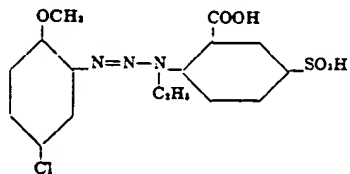
and the labile diazoamino compound which in its free acid state corresponds to the formula



11. A printing preparation containing the 4-aryl-azo-1-amino-7-hydroxynaphthalene of the formula

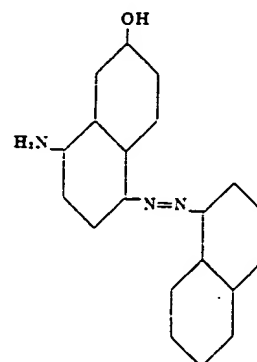


and the labile diazoamino compound which in its free acid state corresponds to the formula



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12. A printing preparation containing the 4-aryl-azo-1-amino-7-hydroxynaphthalene of the formula

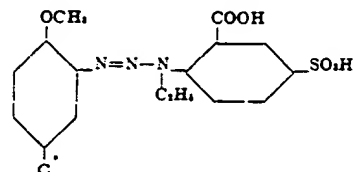


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20 and the labile diazoamino compound which in its free acid state corresponds to the formula



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